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(54) CARBON MATERIAL AND ITS PRODUCTION, NEGATIVE POLE FOR LITHIUM SECONDARY BATTERY AND LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To produce a carbon material for achieving a lithium secondary battery high in initial efficiency and also large in discharge capacity.

SOLUTION: The carbon material contains a carbonaceous material and at least one kind among metals capable of forming alloys with lithium or their compds. As one form of the carbon material, for example, the carbonaceous material contains at least one kind metal capable of forming the alloy with lithium. The other form of the carbon material is, for example, a mixture of the carbonaceous material with at least one kind metal capable of forming the alloy the lithium. Here, the metal capable of forming the alloy with lithium is, for example, at least one kind selected from the group consisting of calcium, strontium, barium, iridium, silver, cadmium, mercury, boron, aluminum, gallium, indium, thallium, silicon, tin, lead, antimony, bismuth and tellurium.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] This invention relates to a carbon material and a carbon material available as a negative-electrode material for lithium secondary batteries especially.
[0002]
[Description of the Prior Art] Development of a lightweight rechargeable battery is demanded by small [for driving such portable electrical machinery and apparatus] by the end of today when the miniaturization of the portable electronic devices represented by a cellular phone, portable information machines and equipment (for example, the so-called electronic notebook and the so-called portable personal computer), etc., thin-shape-izing, and lightweight-ization are progressing splendidly. Under such a background, it can constitute small, the lithium secondary battery which moreover has high energy density attracts attention, and the development is performed briskly. Incidentally, a possibility of having a bad influence on environment is small, and it not only says that a lithium secondary battery can only be miniaturized, but since safety is also high, recently, the expansion as a distributed process input output equipment cell for stationary energy storage is expected as a cell for electric vehicles.
[0003] By the way, the thing using foil-like a lithium and a lithium alloy as a negative-electrode material for lithium secondary batteries is known for many years. However, what used the lithium for the negative electrode has the defect that the cycle life of charge and discharge is short, in order that an arborescence lithium (dendrite) may generate to a negative electrode and this may cause the short circuit between a positive electrode and a negative electrode as charge and discharge are repeated. On the other hand, a crystal structure changes with receipts and payments of the lithium ion accompanying charge and discharge a lot, and what used the lithium alloy for the negative electrode originates in the volume change by the expansion and contraction in that case, and has the defect that the cycle life of charge and discharge is short, like the case where a lithium is used for a negative electrode.
[0004] Then, the carbon material in which insertion and desorption of a lithium ion are possible is proposed as a negative-electrode material for lithium secondary batteries which can raise the cycle property of charge and discharge, and this is becoming in use now. The negative-electrode material for lithium secondary batteries which consists of a carbon material can mainly be classified into two kinds such as the thing of a carbon system with small crystallinity, and the thing of a graphite system with big crystallinity. Here, if the negative-electrode material of a graphite system incorporates a lithium ion at the time of charge and discharge, it will become the compound in which a presentation is shown by C6Li, and theoretical charge-and-discharge capacity will become 372 Ah/kg. This value is 1/10 or less as compared with 3,800 Ah/kg which is the theoretical charge-and-discharge capacity of the lithium itself, and is very small. On the other hand, the negative-electrode material of a carbon system is made realizable compared with the thing of a graphite system in a big charge-and-discharge capacity, for example, the charge-and-discharge capacity of 400 or more Ah/kg. However, since such a negative-electrode material of a carbon system has low conductivity, its overvoltage is large, and its initial effectiveness is as low as 80% order. Incidentally, the initial effectiveness of a negative electrode is an important parameter when a lithium secondary battery is constituted that it is small and cheaply. That is, since more positive-electrode materials are needed to it when the initial effectiveness of a negative-electrode material is low, a lithium secondary battery will become expensive and a lithium secondary battery will be inevitably enlarged from the need of carrying out packing of the positive-electrode material of such many to coincidence.
[0005] The purpose of this invention is to realize the carbon material for attaining the negative electrode for lithium secondary batteries with a big discharge capacity with high and initial effectiveness.
[0006]
[Means for Solving the Problem] A carbon material concerning this invention contains a carbonaceous material and at least one sort in a metal which can form a lithium and an alloy, and its compound. One gestalt of this carbon material contains at least one sort in a metal with which for example, a carbonaceous material can form a lithium and an alloy, and its compound. Moreover, other gestalten of this carbon material are a metal which can form for example, a carbonaceous material, and a lithium and an alloy, and at least one sort in that compound of mixture.
[0007] Here, a metal which can form a lithium and an alloy is at least one sort chosen from a group which consists of calcium, strontium, barium, iridium, silver, cadmium, mercury, boron, aluminum, a gallium, an indium, a thallium, silicon, tin, lead, antimony, a bismuth, and a tellurium. Moreover, for example, a laminating characteristic of a carbonaceous material is the thing of 0.3-0.8.
[0008] The manufacture method of the carbon material concerning this invention includes the production process which prepares the mixture containing a raw material for carbonaceous materials which can be changed into a carbonaceous material by heat-treatment, at least one sort in a metal which can form a lithium and an alloy, and a compound of the metal, and a cross linking agent for constructing a bridge in a raw material for carbonaceous materials, the production process which heat-treat obtained mixture under existence of an acid catalyst, and obtain a carbon precursor, and the production process which carbonize the carbon precursor concerned.
[0009] This manufacture method includes further a production process which carries out non-deliquesce, before carbonizing a carbon precursor. Moreover, a raw material for carbonaceous materials used by this manufacture method is at least one sort in a pitch and tar. Furthermore, a lithium and a metal which can form an alloy used by this manufacture method are at least one sort chosen from a group which consists of calcium, strontium, barium, iridium, silver, cadmium, mercury, boron, aluminum, a gallium, an indium, a thallium, silicon, tin, lead, antimony, a bismuth, and a tellurium.

[0010] Other manufacture methods of a carbon material concerning this invention include a production process which mixes powder of a carbonaceous material, and a metal which can form a lithium and an alloy and at least one sort of powder of the compound.
[0011] A carbonaceous material used here passes a production process including a production process which prepares mixture containing a raw material for carbonaceous materials which can be changed into a carbonaceous material by heat-treatment, and a cross linking agent for constructing a bridge in the raw material for carbonaceous materials concerned, a production process which heat-treats obtained mixture under existence of an acid catalyst, and obtains a carbon precursor, and a production process which carbonizes the carbon precursor concerned. In addition, a raw material for carbonaceous materials used in this case is at least one sort in a pitch and tar.
[0012] A carbon material concerning this invention is used as for example, a negative-electrode material for lithium secondary batteries. A negative electrode for lithium secondary batteries concerning this invention contains a carbon material concerning this invention. A lithium secondary battery concerning this invention is equipped with a negative electrode for lithium secondary batteries concerning this invention.

[0013]
[Embodiment of the Invention] The carbonaceous material used with the carbon material of carbon material this invention will not be limited, especially if the well-known organic substance which can generate carbon by heat-treatment, i.e., the raw material for carbonaceous materials, is heat-treated and it carbonizes. For example, what heated at least one sort of raw materials for carbonaceous materials chosen from the group which consists of melting polymer and phenol resin, such as a coal system pitch, coal system tar, coal system heavy oil, a petroleum system pitch, petroleum system tar, petroleum system heavy oil, and a polyacrylonitrile, and was carbonized is used as a carbonaceous material.
[0014] The thing of the range of 0.3-0.8 has [the above-mentioned carbonaceous material used by this invention] the desirable laminating characteristic (Stacking Index:SI) shown by the following formula (1). In addition, in the formula (1), Im shows the diffraction reinforcement of the field acquired by powder X diffraction measurement (002), and Ia shows the minimum reinforcement near [which is obtained by this measurement] 2 theta= 33 degree.
[0015]
[Equation 1]

$$SI = (Im - Ia) / Im \qquad \cdots (1)$$

[0016] When the laminating characteristic of the carbonaceous material used by this invention is less than 0.3, there is a possibility that the intercalation of a lithium may stop being able to happen easily. On the contrary, when 0.8 is exceeded, in order that a carbonaceous material may approach a graphite system material, there is a possibility that capacity may not fully increase. For the more desirable range of such a laminating characteristic, or more 0.4 0.75 or less and a still more desirable range are [or more 0.5 0.65 or less and the still more desirable range of or more 0.45 0.7 or less and a still more desirable range] usually 0.63 or less [0.55 or more].
[0017] Especially the configuration and gestalt of a carbonaceous material are not limited, and are the shape of the shape of a scale, massive, fibrous, and a whisker, and what [various kinds of] are spherical, such as a letter of crushing. Moreover, the mean particle diameter of such a carbonaceous material usually has desirable about 1-30 micrometers. In addition, a carbonaceous material may be the mixture of the thing of two or more sorts of a configuration and gestalten.
[0018] On the other hand, the metal used with the carbon material of this invention is a metal which can form a lithium and an alloy. As such a metal, the IIA group metallic element in the periodic table of an element, a VIII group metallic element, IB group metallic element, an IIB group metallic element, an IIIB group metallic element, an IVB group metallic element, VB group metallic element, and a VIB group metallic element can be mentioned, for example. Initial effectiveness by among these, the reason for being easy to attain the high negative electrode for lithium secondary batteries with a big capacity The potassium, strontium, and barium which are an IIA group metallic element, The iridium which is a VIII group metallic element, the silver which is IB group metallic element, the cadmium which is an IIB group metallic element, and mercury, The boron which is an IIIB group metallic element, aluminum, a gallium, an indium, and a thallium, It is desirable especially to use at least one sort chosen as the silicon which is an IVB group metallic element, tin and lead, the antimony that is VB group metallic element and the bismuth, and the list from the group which consists of a tellurium which is a VIB group metallic element.
[0019] In addition, the metal which can form the above lithiums and alloys may be contained in the carbon material of this invention as the metal itself, and may be contained in the carbon material of this invention as metallic compounds. Of course, the metal itself and metallic compounds may be contained in coincidence. Namely, at least one sort in an above-mentioned metal and its compound should just be used. Here, as metallic compounds, an organic-acid salt (for example, acetate), an inorganic-acid salt (for example, a chloride, a carbonate, a nitrate), carbide, a nitride, etc. of the various above metals can be mentioned. Hereafter, at least one sort of things of an above-mentioned metal and its compound may be named generically, and it may only be called a "metal."
[0020] The carbon material of this invention can be classified according to the content condition of the above-mentioned metal which can form a lithium and an alloy. That is, when the above-mentioned carbonaceous material contains the above-mentioned metal which can form a lithium and an alloy in the interior (gestalt 1), it can classify into two kinds in the case (gestalt 2) of being the mixture of an above-mentioned carbonaceous material and an above-mentioned metal. However, it is desirable to usually set a metaled content to 0.1 - 25% of the weight of the whole carbon material of this invention in [any] the case of a gestalt. When a metaled content is less than 0.1 % of the weight and it uses the carbon material of this invention as a negative-electrode material for lithium secondary batteries, there is a possibility that the negative electrode for lithium secondary batteries with a big capacity with high and initial effectiveness may be unrealizable. On the contrary, when exceeding 25 % of the weight, there is a possibility that a cycle property may fall.
[0021] In addition, it is more desirable to set up to 20 or less % of the weight 1% of the weight or more among above-mentioned ranges, as for a metaled content, it is still more desirable to set up to 15 or less % of the weight 2% of the weight or more, and it is still more desirable to set up to 10 or less % of the weight 3% of the weight or more. As a metaled content, especially a desirable range is 4 % of the weight or more (preferably 5 % of the weight or more), and is 10 or less % of the weight.
[0022] Incidentally, when the carbon material of this invention contains an above-mentioned metal as metallic compounds, the content of an above-mentioned metal is the value of metallic element conversion.
[0023] The carbon material of manufacture method this invention of a carbon material can be manufactured according to two kinds of methods as follows corresponding to an above-mentioned gestalt.
(The manufacture method 1) By this manufacture method, the mixture containing the raw material for carbonaceous materials, a metal or

metallic compounds (in the explanation about this manufacture method 1, it may only be hereafter expressed as "metallic compounds"), and a cross linking agent is prepared first.
[0024] The raw material for carbonaceous materials used here is a thing as stated above, only one kind of thing may be used independently, and two or more sorts of things may be used together. A thing desirable as a raw material for carbonaceous materials used here incidentally is at least one sort in a pitch and tar at the point which is low cost. Moreover, a metal is an above-mentioned metal (for example, powder-like thing) which can form a lithium and an alloy, and, on the other hand, metallic compounds are the metallic compounds of previous statement of the above-mentioned metal which can form a lithium and an alloy. Only one kind of thing may be used independently, respectively, and, as for such a metal and metallic compounds, two or more sorts of things may be used together. Moreover, a metal and metallic compounds may be used together. furthermore, a thing for a cross linking agent to construct a bridge in the raw material for carbonaceous materials -- it is -- two various organic functions or the polyfunctional compound of three or more organic functions -- one sort of a polyfunctional aromatic compound or two sorts or more are used preferably. In addition, as for a polyfunctional compound, what has for example, a halogenated-aliphatics radical (preferably halogenation methyl group), an alcoholic hydroxyl group, a halogenation carbonyl group, an aldehyde group, and an alkoxy group (preferably methoxy group) is desirable as a functional group.
[0025] As an available cross linking agent, here, for example In addition, aromatic series dimethylene halide, such as xylene dichloride, Aromatic series dimethanol, such as a xylene glycol, terephthalic-acid chloride, Aromatic series dicarbonyl halide, such as isophthalic acid chloride, phthalic-acid chloride and 2, and 6-naphthalene dicarboxylic acid chloride, A benzaldehyde, a p-hydroxy benzaldehyde, para methoxybenzaldehyde, Aromatic series acetals, such as aromatic aldehyde, such as 2, 5-dihydroxy benzaldehyde, a terephthal aldehyde, an isophthal aldehyde, and salichlaldehyde, and a benzaldehyde dimethyl acetal, can be mentioned.
[0026] Especially the preparation method of above-mentioned mixture is not limited, and if it is the method of mixing a component to homogeneity, various kinds of well-known methods can be used for it. For example, when the raw material for carbonaceous materials is what presents the shape of liquid at the time of heating, metallic compounds and a cross linking agent can be added to the raw material for carbonaceous materials which was heated and was made liquefied, and these can be mixed to homogeneity. Moreover, in this case, metallic compounds and a cross linking agent can be added to the raw material for carbonaceous materials before heating, the raw material for carbonaceous materials can be heated after that, and it can be made liquefied, and can also mix to homogeneity.
[0027] In the case of such a mixed method, you may be added to the raw material for carbonaceous materials in the state of powder, and metallic compounds may be added to the raw material for carbonaceous materials, where a predetermined solvent is dissolved or distributed. However, the direction which adopts the latter method is usually desirable from the ability to obtain the more uniform mixture of the raw material for carbonaceous materials, and metallic compounds.
[0028] Although the solvent used in order to dissolve or distribute metallic compounds can be suitably chosen according to the class of metallic compounds, carboxylic acids, such as nitrogen-containing aromatic compounds, such as a quinoline, and an acetic acid, are usually preferably used for an organic solvent especially a polar solvent, and a concrete target. When using an acetic acid as an acid catalyst, for example in the production process concerned depending on the class of acid catalyst used in the production process for incidentally obtaining a carbon precursor which is mentioned later, the acid catalyst concerned itself can also be used as a solvent for dissolving or distributing metallic compounds.
[0029] In an above-mentioned mixed method, the temperature in the case of heating the raw material for carbonaceous materials can be suitably set up in the range which the raw material for carbonaceous materials does not decompose. for example, the case where a pitch or tar is used as a raw material for carbonaceous materials -- heating temperature -- usually -- 100 degrees C or more 350 degrees C or less 150 degrees C or more 300 degrees C or less are more preferably set as 200 degrees C or more 280 degrees C or less.
[0030] In the above-mentioned mixture prepared at this production process, it is desirable to set up so that the content of the above-mentioned metal contained in the carbon material concerning this invention may become an above-mentioned range, the mixed rate of metallic compounds to the raw material for carbonaceous materials usually taking into consideration the carbonization yield of the raw material for carbonaceous materials in the carbonization production process mentioned later. although the mixed rate of a cross linking agent can be suitably adjusted in the large range on the other hand according to the property for which the carbonaceous material which constitutes the carbon material of this invention is asked, for example, a laminating characteristic, microcrystal size, a lattice constant, etc. -- usually -- the weight average molecular weight of the raw material for carbonaceous materials -- 0.01 mols or more five mols or less are preferably set as 0.05 mols or more three mols or less.
[0031] Next, a carbon precursor is prepared from the mixture obtained according to the above-mentioned production process. Here, the obtained mixture is heat-treated under existence of an acid catalyst, and the target carbon precursor is obtained.
[0032] The acid catalyst used at this production process is for promoting the crosslinking reaction of the raw material for carbonaceous materials by the cross linking agent, and it can use various kinds of things, without being limited especially if it is the acid which has the function which promotes such crosslinking reaction. Specifically, inorganic acids, such as organic acids, such as sulfonic acids and carboxylic acids, a hydrochloric acid, a sulfuric acid, and a nitric acid, can be used.
[0033] In addition, just before heat-treating above-mentioned mixture, you may be added by the mixture concerned, and in case an acid catalyst prepares mixture, it may be added by coincidence. As for the amount of the acid catalyst used, it is desirable to usually be set up to 0.5 - 10% of the weight on the basis of the raw material for carbonaceous materials contained in mixture, and it is more desirable to be set up to 1 - 5% of the weight. When the amount of the acid catalyst used is less than 0.5 % of the weight, there is a possibility that the crosslinking reaction of the raw material for carbonaceous materials may become is hard to be promoted. On the contrary, when it exceeds 10 % of the weight, a possibility that an acid catalyst may remain as an impurity is in the carbon material of this invention.
[0034] It is the temperature requirement which can promote the crosslinking reaction of the raw material for carbonaceous materials by the cross linking agent, and the polycondensation reaction of the raw material for carbonaceous materials, as for the laying temperature at the time of the heat-treatment in this production process, it is desirable to usually set it as 250 degrees C or more 400 degrees C or less, and it is still more desirable to set it as 280 degrees C or more (preferably 300 degrees C or more) 350 degrees C or less. When laying temperature is less than 250 degrees C, crosslinking reaction and a polycondensation reaction stop being able to go on easily, and there is a possibility that a carbon precursor may become is hard to be obtained from mixture. On the contrary, when exceeding 400 degrees C, there is a possibility that the raw material for carbonaceous materials may decompose. Incidentally, in the carbonization production process mentioned later, the carbonaceous material which has a laminating characteristic in the above specific ranges is obtained by making the raw material for carbonaceous materials construct a bridge.
[0035] The method of heating, while blowing inert gas, such as the method and nitrogen which are heated while blowing activated gas,

such as oxygen and ozone, as the heat-treatment method of mixture to the method and mixture which distill mixture, for example, and an argon, is employable.
[0036] The carbon precursor pass the above heat-treatment production processes is heat-treated further next, and is carbonized. Thereby, a carbon precursor is changed into a carbonaceous material and the target carbon material is obtained. Under the present circumstances, non-deliquesce processing of the carbon precursor may be carried out beforehand. When performing non-deliquesce processing to a carbon precursor, a carbon precursor is heated in oxidizing atmospheres, such as air. As for the heating temperature in this case, it is desirable to set it as 150 degrees C or more 400 degrees C or less, and it is usually more desirable to set it as 200 degrees C or more 300 degrees C or less. It may be controlled by such non-deliquesce processing that a carbon precursor carries out heat weld mutually in a carbonization production process.
[0037] In case a carbon precursor is carbonized, a carbon precursor is heat-treated in a non-oxidizing atmosphere. As for the heating temperature in this case, it is desirable to set it as 800 degrees C or more 1,500 degrees C or less, and it is usually more desirable to set it as 1,000 degrees C or more 1,300 degrees C or less. When heating temperature is less than 800 degrees C, carbonization of a carbon precursor cannot advance easily and there is a possibility that carbonization yield may fall. On the contrary, when it exceeds 1,500 degrees C, there is a possibility that the capacity as a negative-electrode material for lithium secondary batteries may fall.
[0038] In addition, the carbon precursor may be beforehand processed into desired configuration and gestalten, such as the shape of fibrous, powder, and a particle, before the heat-treatment for the above carbonization. Incidentally, as for such processing, it is usually desirable to carry out before the non-deliquesce processing above-mentioned [to a carbon precursor].
[0039] The carbon material manufactured by the above manufacture methods contains the above-mentioned metal with which a lithium and an alloy can be formed in the interior, above-mentioned carbon material, i.e., carbonaceous material, of a gestalt 1. Since this carbon material is preparing the mixture which made homogeneity distribute metallic compounds to the raw material for carbonaceous materials in an above-mentioned manufacturing process, the metal which can form a lithium and an alloy into a carbonaceous material is distributed by homogeneity.
[0040] (The manufacture method 2) By this method, the carbonaceous material prepared beforehand and at least one sort in the compound (metallic compounds) of the metal which can form a lithium and an alloy, and the above metals concerned are mixed. The carbonaceous material used by this manufacture method is a carbonaceous material obtained like the above-mentioned manufacture method 1, without using the metal which can form a lithium and an alloy, and its compound. Moreover, in addition to this, what carbonized organic substances, such as carbon black, vinylidene chloride resin, sugar, a cellulose, acetone furfural resin, phenol formaldehyde resin, and charcoal, according to the conventional method, and the thing carbonized after carrying out non-deliquesce with a conventional method preferably can also be used.
[0041] As a method of mixing at least one sort in the metal which can form a carbonaceous material, and an above-mentioned lithium and an above-mentioned alloy, and its compound How to mix beforehand fibrous, powdered or the carbonaceous material processed in the shape of a particle etc. and an above-mentioned metal, and at least one sort of powder of the compound in a manufacture process, The method of mixing, while grinding at least one sort in a carbonaceous material, an above-mentioned metal, and its compound in a list is employable.
[0042] As a mixer used when mixing at least one sort in a carbonaceous material, a metal, and its compound, a NAUTA mixer and a ribbon blender can be mentioned, for example. As grinding and a mixer used on the other hand when mixing grinding at least one sort in a carbonaceous material, a metal, and its compound, a ball mill, a hammer mill, CF mill, an atomizer mill, etc. can be mentioned, for example.
[0043] In addition, at least one sort in a carbonaceous material, a metal, and its compound of mixed rates are set up like the case of the above-mentioned manufacture method 1. The carbon materials manufactured by the above manufacture methods are the metal which can form a carbon material, i.e., a carbonaceous material, and the above-mentioned lithium and above-mentioned alloy of a gestalt 2, and at least one sort in the compound of mixture.
[0044] The carbon material of negative-electrode this invention for lithium secondary batteries can be used as the active material, i.e., the negative-electrode material, of the negative electrode for lithium secondary batteries. For example, if the carbon material of this invention is fabricated combining the charge collector (terminal) which consists of a metal with a conventional method, it can constitute the negative electrode for lithium secondary batteries.
[0045] When forming the negative electrode for lithium secondary batteries using the carbon material of this invention, usually the carbon material and resin dispersant of this invention are mixed, a paste is prepared, and this paste is applied to a charge collector. In this case, as a resin dispersant used, fluororesins, such as polyvinylidene fluoride resin and polytetrafluoroethylene resin, various kinds of polyolefine system resin, and various kinds of synthetic rubber are distributed in organic solvents, such as N-methyl pyrrolidone, for example.
[0046] Although especially the content of the resinous principle under paste is not limited, it is desirable to set below to 20 weight sections more than 3 weight sections by solid content conversion to the carbon material 100 weight section, and it is usually more desirable to set below to 10 weight sections more than 5 weight sections. When the rates of a resinous principle are under 3 weight sections, a possibility that exfoliation of an electrode may arise is in charge and discharge. On the contrary, when exceeding 20 weight sections, there is a possibility of reducing the charge-and-discharge capacity as the whole electrode.
[0047] The lithium secondary battery of lithium secondary battery this invention is mainly equipped with the container (case) for containing a positive electrode, a negative electrode, an electrolyte, and these, and can form it in the configuration of requests, such as cylindrical, a square shape, and a carbon button mold. In addition, this lithium secondary battery may be equipped with the gasket or the obturation board if needed.
[0048] Applying [and] what the positive electrode mixed active materials, such as an oxide containing a lithium, $LiCoO_2$ and $LiNiO_2$, or $LiMn_2O_4$, and a well-known binder here, and was made into the shape of a paste on charge collectors, such as metal, a negative electrode is an above-mentioned negative electrode for lithium secondary batteries formed using the carbon material concerning this invention. [for example,] Furthermore, impregnation of the electrolyte is carried out to the separator which consists of polyolefin resin system porous membrane for being the electrolytic solution which dissolved the salt in organic solvents, such as for example, an aprotic organic solvent, and being arranged between the positive electrode and the negative electrode, for example, preventing the short circuit of a positive electrode and a negative electrode, such as a nonwoven fabric made of porosity polypropylene resin, and it is held.
[0049] The salt which can generate anions which cannot carry out a solvation easily, such as $LiPF_6$, $LiClO_4$, $LiBF_4$, LiAsF6, LiSbF6, $LiAlO_4$, $LiAlCl_4$, LiCl, and LiI, as a salt which constitutes an above-mentioned electrolyte, for example can be used. On the other hand as

an aprotic organic solvent, for example Ethylene carbonate, Propylene carbonate, butylene carbonate, dimethyl carbonate, Ester, such as diethyl carbonate, methylethyl carbonate, and gamma-butyrolactone Furans, such as a tetrahydrofuran and 2-methyl tetrahydrofuran Dioxolane, 4-methyl dioxolane, diethylether, wood ether, Ether, such as 1, 2-dimethoxyethane, diethoxy ethane, and methoxyethoxy ethane, Methyl acetate etc. can be mentioned to dimethyl sulfoxide, a sulfolane, a methyl sulfolane, an acetonitrile, N.N-dimethylformamide, a diethylene glycol, and a methyl formate list. As for these aprotic organic solvents, two or more sorts may be used together.

[0050] In addition, the lithium secondary battery of this invention is replaced with the above-mentioned electrolytic solution, and when a well-known inorganic solid electrolyte, a well-known solid polymer electrolyte, etc. are used, it can be carried out similarly.

[0051] Since the negative electrode is formed using the carbon material of this invention, compared with the conventional thing, initial effectiveness is high, and the lithium secondary battery of this invention has a large charge-and-discharge capacity, and, moreover, its charge-and-discharge cycle property (life) is good. The negative electrode in which this shows high conductivity to since the carbon material of this invention contains the metal which can form ** lithium and an alloy, and discharge capacity with it is shown is realizable, [a low overvoltage and] [high] ** Since a volume change can absorb the volume change by change of the crystal structure produced in case the metal which can form a lithium and an alloy forms a lithium and an alloy in a charge-and-discharge process with a small carbonaceous material, Especially when the laminating characteristic of that it can contribute to improvement in the cycle property of a negative electrode and ** carbonaceous material is an above-mentioned range, it thinks because the features, like the charge-and-discharge capacity and the cycle property of a negative electrode can be raised can be demonstrated in multiplication.

[0052] Since the capacity and initial effectiveness of a negative electrode are high as mentioned above, the lithium secondary battery of this invention can control the amount of active materials of a positive electrode. For this reason, since it is not necessary to use the large-sized container for holding a lot of positive active material, this lithium secondary battery can be miniaturized, maintaining capacity compared with the conventional thing.

[0053]

[Example] Pitch (weight average molecular weight = about 1,000) 500g whose softening temperature which does not contain example 1 (preparation of carbon material) quinoline insoluble is 68.2 degrees C, dimethyl paraxylene glycol (cross linking agent) 30g, and 10g (acid catalyst) of Para toluenesulfonic acid were prepared in the 1l. small reactor, and it was made to heat and dissolve in 250 degrees C. And 10.0g of powder-like silver acetate was added gradually, stirring the contents of a small reactor, and stirring was continued after addition termination for further 0.5 hours.

[0054] Next, heating the pitch in a small reactor at 330 degrees C, and stirring under ordinary pressure, air was blown for 240 minutes at 5l. a rate for /, and the polycondensation of the pitch was carried out. When this was cooled to the room temperature, the carbon precursor (solid-like carbon) was obtained. This carbon precursor was ground using the ball mill, then supplying air at 2l. a rate for /, with 2-degree-C programming rate for /, to 300 degrees C, it heated and non-deliquesce processing of this was carried out. Using the usual heat treating furnace, in the nitrogen air current, the carbon precursor by which non-deliquesce processing was carried out was heated to 1,100 degrees C, and was held for 2 hours. Consequently, the carbon precursor was carbonized and the carbon material was obtained.

[0055] After putting in coal tar 1,000g which removed completely example 2 (preparation of carbon material) quinoline insoluble in the distilling flask and setting the inside of a flask as nitrogen-gas-atmosphere mind, the coal tar was warmed at 50-70 degrees C. On the other hand, 15.0g of silver acetate was added in the beaker containing a 100ml quinoline, and it was made to dissolve in ordinary temperature.

[0056] The contents of a beaker were gradually dropped into the coal tar currently warmed within the flask, and it stirred for about 0.5 hours. Then, when the contents of a flask were distilled under reduced pressure and a part for a quinoline and the elasticity in a coal tar was removed, the pitch (weight average molecular weight = about 1,200) whose softening temperature is 82.6 degrees C was obtained.

[0057] Obtained pitch 500g, dimethyl paraxylene glycol (cross linking agent) 30g, and 10g (acid catalyst) of Para toluenesulfonic acid were prepared in the 1l. small reactor, and it dissolved at 250 degrees C. And 10.0g of powder-like silver acetate was added gradually, stirring the contents of a small reactor, and stirring was continued after addition termination for further 0.5 hours.

[0058] Next, heating the pitch in a small reactor at 330 degrees C, and stirring under ordinary pressure, air was blown for 240 minutes at 5l. a rate for /, and the polycondensation of the pitch was carried out. When this was cooled to the room temperature, the carbon precursor (solid-like carbon) was obtained. This carbon precursor was ground using the ball mill, after that, non-deliquesce processing and heat-treatment (carbonization processing) were carried out like the case of an example 1, and the carbon material was obtained.

[0059] Pitch (weight average molecular weight = about 1,000) 500g whose example 3 (preparation of a carbon material) softening temperature is 68.2 degrees C, dimethyl paraxylene glycol (cross linking agent) 30g, and 10g (acid catalyst) of Para toluenesulfonic acid were prepared in the 1l. small reactor, temperature was adjusted to 150-170 degrees C, and the pitch was dissolved. On the other hand, quinoline 50ml containing 0.1% of the weight of an acetic acid is taught in a beaker, and 15.0g of silver acetate was added to this, and it was made to dissolve in it at 70-80 degrees C.

[0060] Within the small reactor, the contents of a beaker were gradually dropped into the pitch currently warmed by 150-170 degrees C, and it stirred for about 0.5 hours. Then, heating the pitch in a small reactor at 330 degrees C, and stirring under ordinary pressure, air was blown for 240 minutes at 5l. a rate for /, and the polycondensation of the pitch was carried out. When this was cooled to the room temperature, the carbon precursor (solid-like carbon) was obtained. This carbon precursor was ground using the ball mill, after that, non-deliquesce processing and heat-treatment (carbonization processing) were carried out like the case of an example 1, and the carbon material was obtained.

[0061] The softening temperature which does not contain example 4 (preparation of carbon material) quinoline insoluble prepared pitch (weight average molecular weight = about 1,000) 500g which is 68.2 degrees C, dimethyl paraxylene glycol (cross linking agent) 30g, and 10g (acid catalyst) of Para toluenesulfonic acid in the 1l. small reactor, heated at 250 degrees C, and stirred for 0.5 hours. And raising the temperature in a small reactor to 330 degrees C, and stirring under ordinary pressure, air was blown for 240 minutes at 5l. a rate for /, and the polymerization of the pitch was carried out. When this was cooled to the room temperature, the carbon precursor (solid-like carbon) was obtained.

[0062] The obtained carbon precursor was ground using the ball mill, then supplying air at 2l. a rate for /, with 2-degree-C programming rate for /, to 300 degrees C, it heated and non-deliquesce processing of this was carried out. Using the usual heat treating furnace, in the nitrogen air current, the carbon precursor by which non-deliquesce processing was carried out was heated to 1,100 degrees C, and was held for 2 hours. Consequently, the carbon precursor was carbonized and the carbonaceous material was obtained.

[0063] To 18g of obtained carbonaceous materials, 2g was mixed in the end (product made from incorporated company rare metallic) of

silver dust whose mean particle diameter is 1-2 micrometers, the planet-type ball mill was used, this mixture was fully stirred and ground, and the carbon material with which a carbonaceous material and the end of silver dust were mixed by homogeneity was obtained.
[0064] It was operated like the case of an example 1, without using example of comparison 1 (preparation of a carbon material) silver acetate, and the carbon material was obtained.
[0065] The carbon material 92 weight section obtained, respectively in the evaluation examples 1-4 and the example 1 of a comparison was mixed with the polyvinylidene fluoride resin 8 weight section, and this was dissolved in N-methyl pyrrolidone of optimum dose, it stirred, and slurry-like mixture was obtained. After having used the doctor blade, applying this slurry-like mixture on electrolytic copper foil and drying for 30 minutes at 110 degrees C, it pressed using the roll press machine and the negative electrode for lithium secondary batteries was obtained. The electrode of 2 was cut down 1cm from this negative electrode, and it considered as the test electrode. The vacuum drying of 6 hours was performed at 200 degrees C to this test electrode.
[0066] For the comparison, it replaced with the carbon material and ** for tales doses and the same test electrode were created for the end of silver dust (the product made from incorporated company rare metallic: in the next table 1, it is the negative-electrode material displayed as "an example 2 of a comparison") whose mean particle diameter is 1-2 micrometers.
[0067] The lithium secondary battery was further produced for the propylene carbonate solution which contains [the test electrode obtained as a negative electrode] LiClO4 for enough lithium metals of an amount by the concentration of one mol/l. as the electrolytic solution to the negative electrode concerned as a counter electrode as a separator, using a polypropylene resin nonwoven fabric respectively.
[0068] About this lithium secondary battery, the charge-and-discharge property (discharge capacity and initial effectiveness) was investigated. Here, constant-potential charge was carried out after 1mA /charges under the constant current conditions of 2 cm and potential amounts to 10mV until voltage is set to 10mV until sum total time amount became in 12 hours. Moreover, under the constant current condition of 1 mA/cm2, discharge was carried out until voltage became more than 1.3V. In addition, charge and discharge measured the discharge capacity of 10 cycle repeat and the 1st cycle eye, and the discharge capacity of the 10th cycle eye. A result is shown in a table 1.
[0069] In addition, in a table 1, a laminating characteristic is the value which carried out analysis by powder X-ray diffractometry to the carbon material obtained in examples 1-4 and the example 1 of a comparison, and was calculated according to the formula (1) as stated above based on the result. incidentally -- the Measuring condition of a powder X diffraction, and the calculation method of a laminating characteristic -- Hiroyuki Fujimoto, Shiraishi ** "carbon" 167,101 (1995), and M.Shiraishi and KKobayashi "Bull. Chem.Soc. Jap." -- it referred to 46, 2575 (1973), and Shiraishi **** Sanada [Yuzo] "Chemical Society of Japan" 1,153 (1976).
[0070]
[A table 1]

表 1

負極材料	積層指数	銀含有量 (重量%)	第1サイクル目放電容量 (Ah／kg)	初期効率 (%)	第10サイクル目放電容量 (Ah／kg)
実施例1	0．57	5．3	472	85	469
実施例2	0．63	6．2	478	84	474
実施例3	0．65	7．8	483	86	481
実施例4	0．58	10．0	491	82	485
比較例1	0．58	0	434	78	429
比較例2	−	100	620	76．2	330

[0071]
[Effect of the Invention] Since the carbon material of this invention contains at least one sort in the metal which can form a lithium and an alloy, and its compound, it can realize the negative electrode for lithium secondary batteries with a big discharge capacity with high and initial effectiveness.
[0072] Moreover, since the carbon material of this invention is used for the negative electrode for lithium secondary batteries of this invention, initial effectiveness is high and its discharge capacity is large.
[0073] Furthermore, since the negative electrode for lithium secondary batteries of this invention is used for the lithium secondary battery of this invention, initial effectiveness is high and its discharge capacity is large.

[Translation done.]